

PATENT SPECIFICATION ⁽¹¹⁾

1 424 425

1 424 425

- (21) Application No. 27679/73 (22) Filed 11 June 1973
 (31) Convention Application No. 261809 (32) Filed 12 June 1972 in
 (33) United States of America (US)
 (44) Complete Specification published 11 Feb. 1976
 (51) INT CL² B32B 27/06 B05D 1/36 1/38 B32B 27/32 27/36



(52) Index at acceptance

B2E	208	209	228	233	236	238	23Y	242	243	244	245	246	268	285
	286	287	28Y	296	29Y	305	306	307	313	317	31Y	327	346	
	347	34Y	368	373	375	378	37Y	410	41X	41Y	439	44Y	463	
	464	46Y	498	50X	532	588	598	620	626	628	62X	62Y	65Y	
	673	677	67Y	707	708	70Y	718	743	74Y	755	756	757	767	
	768	76Y	785	787	788	79Y	B5N	2706	2716					

(72) Inventors: JAMES LEE HECHT, RALPH KINGSLEY ILER

(54) COATED ORGANIC POLYMERIC FILMS

(71) We, E. I. DU PONT DE NEMOURS AND COMPANY, a Corporation organised and existing under the laws of the State of Delaware, United States of America, located at Wilmington, State of Delaware, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates to organic polymeric films having a lithium silicate-containing coating on at least one surface thereof to provide a moisture and gas barrier layer.

In the preparation of thermoplastic polymeric films and similar articles, it is often necessary to modify the permeability or surface characteristics of the finished product to impart characteristics not exhibited by the film itself. Accordingly many different classes of coating materials have previously been used to modify the characteristics of thermoplastic materials. Of the inorganic materials used for coating, continuous, glassy coatings are known to provide excellent moisture and gas barrier properties. However, such materials are generally difficult to apply to the polymer surface.

The present invention provides coated films having good moisture and gas impermeability which are easily and economically prepared.

Specifically the invention provides a water-insensitive organic, polymeric film having a substantially continuous gas and liquid-impermeable coating on at least one surface thereof, the coating comprising from 0.1 to 0.6 g./m² of lithium silicate having a mole ratio of SiO₂ to Li₂O of from 1.6/1 to 4.6/1.

Preferably, coated films of the invention further comprise a heat-sealable polymeric coating applied over the silicate coating.

The coated films can be prepared by applying to at least one surface of the uncoated film an aqueous dispersion of lithium silicate having a mole ratio of SiO₂ to Li₂O of from 1.6/1 to 4.6/1, and drying the coated article at an elevated temperature to remove water.

Films for coating in this invention can be prepared from, for example, polyesters, polyolefins such as polypropylene or polyethylene or copolymers thereof including ionomers, the perfluoro polymer prepared from tetrafluoroethylene and hexafluoropropylene, polyacrylonitrile, polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polystyrene, polyimides, or polyamides. Of these, polyester films such as oriented heat set polyethylene terephthalate and oriented linear polypropylene films are particularly preferred. The polymer used as a base in the present invention is water-insensitive. That is, the polymer should not undergo a substantial change in dimension or structural integrity when exposed to the aqueous dispersion that can be used to apply the barrier coatings in accordance with the invention.

The coatings of the invention consist essentially of lithium silicate. It has been found that these coatings provide excellent gas and moisture barrier properties for thermoplastic films when the mole ratio of SiO₂ and Li₂O is from 1.6/1 to 4.6/1. In addition, it has been found that particularly satisfactory barrier properties are obtained with SiO₂/Li₂O mole ratios of from 3.2/1 to 4.2/1, and such coatings are therefore particularly preferred.

According to the organic invention, the lithium silicate can be applied to the polymeric film in the form of an aqueous colloidal dispersion. The dispersion can be prepared from available lithium silicate compositions, such as that commercially available from E. I. du Pont

BEST AVAILABLE COPY

de Nemours and Company as "Lithium Polysilicate 48". This composition is an aqueous solution of $\text{SiO}_2/\text{Li}_2\text{O}$ having a ratio of about 4.8/1 and having about 20% by weight of SiO_2 . This composition, after dilution with water to the desired solids content, can be adjusted as to $\text{Li}_2\text{O}/\text{SiO}_2$ ratio by the addition of lithium hydroxide. After the addition of the required amount of lithium hydroxide, for best barrier properties, the mixture can be heated, for example, to 70°C ., and maintained at this temperature for 1/2 hour, and then cooled to room temperature.

The concentration of the dispersion is not critical to the invention and can be adjusted to satisfy the requirements of coating apparatus used and final coating thickness desired. In general, the dispersions have a solids content of less than 8%, when used with kiss or doctor roll coating techniques.

The colloidal dispersion can also contain additives such as resins that improve the wettability and adhesion of the coatings to the base to which they are applied. Adhesion promoting additives which have been found particularly effective in this application include melamine-formaldehyde resins, urea-formaldehyde resins, polyethylenimine, and amino acids such as glycine and alanine alone or in combination. In general, up to 50%, by weight of the silicate, of such adhesion promoting additives can be used in the coating. The adhesion promoting additive is conveniently incorporated into the dispersion after the adjustment to the required mole ratio.

The dispersion can be coated onto one or both sides of the film using any conventional coating technique including, for example, kiss coating, doctor rolls, gravure rolls, immersion coating techniques, or spraying, with or without such expedients as Mayer rods or air doctor knives. The dispersion is preferably applied to the polymeric film within a week after preparation, since extended aging of the dispersion depreciates its barrier properties. The coating thickness should be such as to give 0.1 to 0.6 g./m.² of the lithium silicate on the coated surface. The dispersion can be applied, for better adhesion, to a film that has been treated to ionize the surface. Treatments which can be used include flame treatment, electrical discharge treatment, as well as caustic or alkaline etching of the substrate surface. In general, pretreatment by conventional flame treatment is preferred. However, when a resin additive is used in the dispersion, the need for ionization of the base surface is frequently eliminated.

After application of the dispersion, the coated film is dried at elevated temperatures to remove water from the dispersion. Drying times and temperatures will vary widely, depending, for example, on the composition of the base polymeric film, the concentration of the coating sol, the coating thickness, and the air flow in the drier. Coated films are conveniently dried by passing through a tower with radiant heat and countercurrent air flow.

After completion of the drying of the lithium silicate coating, the coated film can be further treated by priming and applying a sealable (e.g. heat-sealable) topcoat of a polymeric material such as polyethylene, vinylidene chloride polymers and copolymers, and ethylene vinyl acetate. Priming agents that can be used include silanes, polyurethanes, aqueous solutions of melamine formaldehyde resins, and aluminium chlorhydroxide. The top coating can be applied by solvent coating, conventional melt extrusion techniques, hot lamination of a preformed film of the heat sealable polymer, or polymer dispersion. It has been found that the barrier properties of films of the invention are often improved when sealable polymer topcoats are applied, beyond the expected additive effect of the two coatings. In addition, the application of a sealable polymer topcoat results in a marked improvement in the retention of barrier properties of the present coatings after repeated flexing. The application of such topcoats is therefore preferred.

The coated articles of the invention, and particularly films, exhibit remarkably improved moisture and gas impermeability. The present coated films are therefore well suited for packaging applications in which moisture and gas impermeability are desired.

Films according to the invention are illustrated schematically in the accompanying drawing (Figures 1 and 2) wherein 1 represents the water-insensitive base film, 2 the lithium silicate coating, and 3 a sealable topcoat.

The invention is further illustrated by the following Examples. The coating thicknesses indicated in the Examples provided a lithium silicate coating within the range 0.1 to 0.6 g/m.².

Examples 1-4

In Examples 1-4, lithium silicate solutions were prepared using "Lithium Polysilicate 48" commercially available from E. I. du Pont de Nemours and Company, containing 20% by weight of SiO_2 and having a $\text{SiO}_2/\text{Li}_2\text{O}$ ratio of about 4.8/1. The solution was diluted with water to varying extents as indicated in Table I, and the $\text{SiO}_2/\text{Li}_2\text{O}$ ratio was adjusted to varying extents by the addition of lithium hydroxide, also as indicated in Table I. The mixtures were heated to 70°C . for 1/2 hour and then cooled to room temperature. The coatings were applied to oriented heat set polyethylene terephthalate film having a thickness of 1.5 mils. The polyethylene terephthalate films were flame treated prior to coating with oxidizing or reducing flames having a ratio of propane to oxygen of from 0.95 to 1.10. The coating solutions were

BEST AVAILABLE COPY

applied by a doctor roll at varying speeds and thicknesses. The coating thickness in each case was determined by the conventional ash method.

Additional samples of the films were laminated to low density polyethylene films, having a thickness of 2 mils, after treatment to promote adhesion.

5 The film samples were all dried and tested for oxygen and moisture permeability, and the results indicated in Table I. 5

10 The coated film of Example 2 was subjected to 20 flexes in accordance with the Gelbo flex test, and the oxygen permeability after testing is indicated in Table I. In addition, the oxygen permeability of those samples additionally laminated to polyethylene and subjected to 20 flexes in the Gelbo flex test was determined and these results additionally indicated in Table I. 10

The oxygen permeability of Examples 1-4, together with the permeability of other examples of the invention similarly prepared as well as illustrative control samples, is graphically illustrated in Figure 3 of the drawing (the oxygen permeability units are cc./645 cm.²-24 hrs. for a pressure differential of 1 atmosphere).

BEST AVAILABLE COPY

TABLE 1

Example	% Solids in Bath	SiO ₂ /Li ₂ O Ratio	Coating Speed (fpm)	Coating Thickness (4)	Oxygen Permeability (1)		PE Laminate After Flexing (3)		Moisture Permeability (2)	
					Coated Film	After Flexing (3)	Laminate	PE Laminate After Flexing (3)	Coated Film	PE Laminate
1	6.8	3.2	39	1.31	0.12	—	0.14	0.26	8	12
2	3.4	2.5	25	0.54	0.08	0.24	0.09	0.13	28	14
3	3.4	1.8	39	0.87	0.16	—	0.05	0.07	18	13
4	1.7	2.5	39	0.41	9.17	—	0.05	0.19	35	16

(1) CC./100 in.²—24 hrs. atm. for oxygen permeability, as measured on an Ox-Tran 100 available from Moxem Controls, Minneapolis, Minnesota.

(2) Grams/100 m.² hr. water vapor permeation, as measured by the method described in U.S. Patent 2,147,180.

(3) Gelbo Flex Test (according to P. A. Gelber *et al.*, "Modern Packaging", January 1952, page 125).

(4) Units are weight percent of ash residue from film plus coating.

BEST AVAILABLE COPY

Example 5

The general procedure of Examples 1-4 was repeated using a lithium silicate having a $\text{SiO}_2/\text{Li}_2\text{O}$ ratio of 2.5. The film was coated with a 0.3 mil thickness of vinylidene chloride copolymer and tested. The topcoated film was found to exhibit an oxygen permeability of less than 0.05 cc./100 in. ² 24 hrs. atm., and a moisture permeability of 8 grams/100 m.² hr.

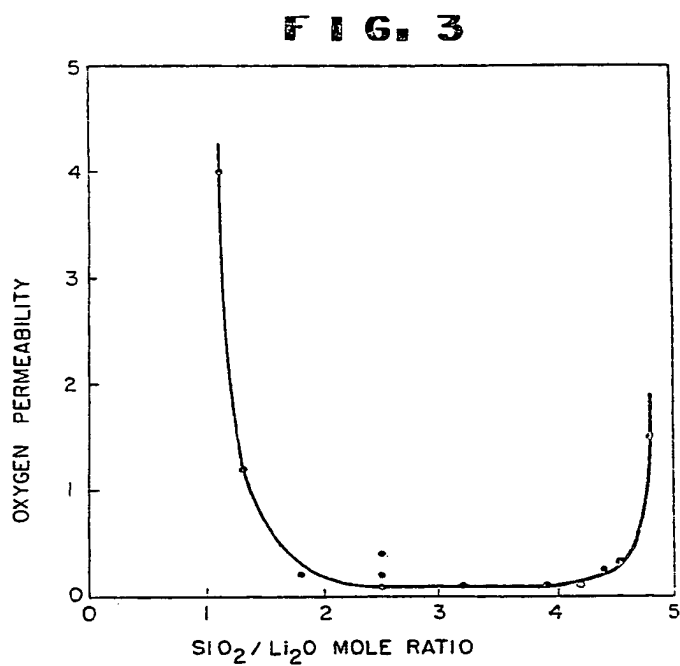
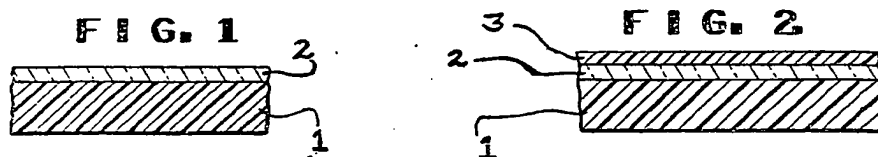
WHAT WE CLAIM IS:—

1. A water-insensitive organic, polymeric film having a substantially continuous gas and liquid-impermeable coating on at least one surface thereof, the coating comprising from 0.1 to 0.6 g./m² of lithium silicate having a mole ratio of SiO_2 to Li_2O of from 1.6/1 to 4.6/1.
2. A film according to claim 1 wherein the coating further comprises up to 50% by weight of the coating, of an adhesion promoting additive selected from melamine-formaldehyde resins, urea-formaldehyde resins, polyethyleneimine, glycine and alanine.
3. A film according to claim 1 or 2 further comprising a sealable polymeric topcoat on at least one surface thereof.
4. A film according to any of claims 1 to 3 wherein the mole ratio of SiO_2 to Li_2O is from 4.2/1 to 3.2/1.
5. A film according to any of claims 1 to 4 wherein the said at least one surface of the film having the lithium silicate-containing coating is flame treated prior to the application of the lithium silicate coating.
6. A water-insensitive organic polymeric film having a lithium silicate coating on at least one surface thereof substantially as herein described in any of Examples 1 to 5.
7. A process for the preparation of a coated film as claimed in claim 1 which comprises applying to at least one surface of the uncoated film an aqueous dispersion of lithium silicate having a mole ratio of SiO_2 to Li_2O of from 1.6/1 to 4.6/1, and drying the coated article at an elevated temperature to remove water.
8. A process according to claim 7 which further comprises flame treating said at least one surface prior to the application of said aqueous dispersion.
9. A process according to claim 7 or 8 which further comprises applying a heat sealable polymeric topcoat to at least one surface of the film.
10. A process for preparing a water-insensitive organic polymeric film having lithium silicate coating on at least one surface of the film, substantially as herein described in any one of Examples 1 to 5.
11. A coated film when prepared by the process of any of claims 7 to 10.

For the Applicant,
CARPMAELS & RANSFORD,
Chartered Patent Agents,
43 Bloomsbury Square,
London WC1A 2RA

Printed for Her Majesty's Stationery Office, by Croydon Printing Company Limited, Croydon, Surrey, 1976.
Published by The Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.

BEST AVAILABLE COPY



BEST AVAILABLE COPY